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**Application of the Mean Spherical Approximation to the Estimation of Single Ion Thermodynamic
Quantities of Solvation for Monoatomic Monovalent Ions in Aqueous Solutions**

by

W. Ronald Fawcett and Lesser Blum

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**Department of Chemistry
University of California
Davis, CA 95616**

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13. ABSTRACT (Maximum 200 words) The expression for the Gibbs energy of solvation for simple 1-1 electrolytes within the mean spherical approximation has been fitted to data for 20 alkali metal halides in water. In performing this fit, one needs to assume a radius for each ion, the Pauling values often having been chosen in the past. The MSA parameters appear as corrections to these radii and are different for cations and anions. Two sets of ionic radii were considered, the Pauling values from crystallographic data and values based on X-ray diffraction results obtained in aqueous solutions. Excellent fits between theory and experiment were obtained, the results with the latter set of radii being preferred. This analysis provides an extrathermodynamic route to single ion solvation free energies and yields results which are very close to the real free energy of solvation measured by Randles.				
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Preliminary Note

Application of the Mean Spherical Approximation to the Estimation of Single Ion Thermodynamic Quantities of Solvation for Monoatomic Monovalent Ions in Aqueous Solutions

W. Ronald Fawcett

Department of Chemistry

University of California

Davis, California 95616, U.S.A.

and

Lesser Blum

Department of Physics, P.O. Box 23343

University of Puerto Rico

Rio Piedras, Puerto Rico 00931, U.S.A.

Introduction

The separation of thermodynamic quantities for electrolytes in solution into contributions for the cation and anion is a well known problem in solution electrochemistry [1]. It has important consequences with respect to the establishment of an absolute potential scale, a subject which has been considered in detail by Trasatti [2, 3] and Parsons [4]. Obviously, an extrathermodynamic assumption is required to achieve this separation and various approaches based on appropriate theories have been considered [1-4].

Very recently, we discussed the application of the mean spherical approximation (MSA) to estimate the Gibbs energies of solvation of monoatomic monovalent ions in polar solvents [5]. According to the MSA model two solvent dependent parameters other than those used in the

classical Born model are required. These are the polarization parameter λ which accounts especially for short range interactions between the solute ion and surrounding solvent dipoles, and r_s the radius of the solvent molecule represented as a sphere. It was shown that the ratio λ/r_s depends on whether the monoatomic ion is an alkali metal ion or a halide ion, and on the nature of the solvent such that it increases with solvent basicity in the case of cations, and with solvent acidity in the case of anions [5].

The purpose of the present paper is to examine further the ability of the MSA model to estimate single ion thermodynamic quantities and thus evaluate its significance as an extrathermodynamic route to these quantities for simple monoatomic ions. In this regard, it is important to have reliable estimates of the radii of the ions. These parameters are most often based on the values given by Pauling [6] which were estimated using crystallographic data. However, in recent years, extensive information has become available regarding the structure of aqueous electrolyte solutions on the basis of neutron and X-ray diffraction experiments. This information has been compiled by Marcus [7] and provides an additional source of ionic size data which can be compared with those proposed by Pauling [6]. The effects of the ionic radii on the estimation of Gibbs solvation energies for single ions, and the resulting MSA parameters are described in the present note.

The Model and Its Application to Thermodynamic Data

On the basis of the MSA [5, 8-10] the standard Gibbs energy of ion, i , in solvent, s , at infinite dilution is given by

$$G_s^0(i) = - \frac{N_0 (z_i e_0)^2}{8\pi \epsilon_0} \left(1 - \frac{1}{\epsilon_s}\right) \frac{1}{(r_i + \delta_s)} \quad (1)$$

where N_0 is the Avogadro constant, e_0 , the electronic charge, z_i , the ionic valence, ϵ_0 , the permittivity of free space, ϵ_s , the dielectric constant of the pure solvent, r_i , the ionic radius, and δ_s , the MSA parameter which depends on the nature of the solvent and whether the ion is a cation or anion. The last quantity is related to the polarization parameter, λ , and solvent radius, r_s , discussed above, by the equation

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$$\delta_s = r_s / \lambda \quad (2)$$

In earlier versions of the MSA, the quantity, λ , was estimated from the Wertheim equation [11] that is, using the relationship

$$\lambda^2 (1 + \lambda)^4 = 16 \epsilon_s \quad (3)$$

However, the resulting estimates of λ do not account for important parts of the short range electrostatic interactions between the ion and surrounding dipoles, that is, the "stickiness" of ion-dipole interactions. These interactions result from higher order moments associated with the electrostatic description of the solvent and from its polarizability. In our recent analysis of Gibbs solvation data for monovalent ions [5], λ , and thus δ_s , were treated as adjustable parameters determined from single ion data reported in the literature [12, 13]. In the present paper we apply this analysis to thermodynamic data for the alkali metal halide salts in water. It should be noted that the quantity estimated by eq. (1) is, strictly speaking, only the ion-dipole portion of the Gibbs solvation energy. Thus, it is assumed in the present treatment that one can avoid explicitly treating contributions from dipole-dipole and short range electrostatic interactions by regarding δ_s as an adjustable parameter whose value accounts for these effects.

The expression for the standard Gibbs energy of solvation of the monovalent salt CA becomes

$$G_s^0(\text{CA}) = - \frac{N_0 e_0^2}{8\pi \epsilon_0} \left(1 - \frac{1}{\epsilon_s}\right) \left[\frac{1}{r_C + \delta_{sC}} + \frac{1}{r_A + \delta_{sA}} \right] \quad (4)$$

where r_C and r_A are the radii of the cation and anion, respectively, and δ_{sC} and δ_{sA} , the corresponding values of the MSA distance, δ_s . It is apparent that, if one knows the values of the ionic radii, only two adjustable parameters namely, δ_{sC} and δ_{sA} , are involved in estimating the Gibbs solvation energy for the salt. This expression was used by Latimer et al. [14] to account for the variation in the Gibbs energy of solvation of the alkali metal halides with size of the component ions but the interpretation of the parameters δ_{sC} and δ_{sA} was quite different. They were regarded as corrections to the Pauling radii necessary so that the Born model could be applied to the problem. Another way of interpreting these quantities with the context of a primitive model is as

effective distances over which the dielectric constant varies from a low value near the ion to the bulk value further away [15].

The entropy of a single ion may be found from the temperature derivative of the Gibbs energy:

$$S_s^0(i) = \frac{N_0(z_i e_0)^2}{8\pi \epsilon_0} \left[\frac{1}{\epsilon_s^2} \frac{d\epsilon_s}{dT} \frac{1}{(r_i + \delta_s)} - \left(1 - \frac{1}{\epsilon_s}\right) \frac{1}{(r_i + \delta_s)^2} \frac{d\delta_s}{dT} \right] \quad (5)$$

Its estimation requires two additional parameters namely the temperature coefficient of the dielectric constant $d\epsilon_s/dT$ which is available from experiment, and the temperature coefficient of the MSA parameter, $d\delta_s/dT$. The first term on the right hand side of eq. (5) may be regarded as giving the contribution to the entropy due to long range electrostatic interactions, and the second, that due to short range interactions. In earlier work [14], the parameter δ_s was considered to be a constant so that an important contribution to the entropy was ignored. Within the context of the MSA, the temperature variation in δ_s is due to a corresponding change in $d\lambda/dT$ (eq. (3)). Since the "stickiness" of ion-solvent interactions are expected to decrease as temperature increases, $d\lambda/dT$ is expected to be a negative quantity and $d\delta_s/dT$, positive. For the same reasons that the relationship between λ and ϵ_s is considered to be more complex than that given by eq. (3), the relationship that could be derived from this equation between $d\lambda/dT$ and $d\epsilon_s/dT$ does not properly account for the change in ion-solvent interactions with temperature.

It is convenient to re-express the single ion entropy in terms of the single ion Gibbs energy. Thus, eq. (5) may be rewritten as

$$S_s^0(i) \left(1 - \frac{1}{\epsilon_s}\right) = - \frac{G_s^0(i)}{\epsilon_s} \frac{d\epsilon_s}{dT} - \frac{8\pi \epsilon_0}{N_0(z_i e_0)^2} [G_s^0(i)]^2 \frac{d\delta_s}{dT} \quad (6)$$

When estimates of $G_s^0(i)$ are available, entropic data for a series of ions may be plotted on the basis of eq. (6) to obtain a value of the parameter $d\delta_s/dT$.

Experimental values of the Gibbs energies of solvation for 20 alkali metal halide salts based on the five cations from Li^+ to Cs^+ and the four anions from F^- to I^- were obtained by adding the

corresponding single ion values from the tabulation by Parsons [4]. The single ion values are those based on the assumption that $G_s^0(H^+) = 0$, and should give the best estimates of the required electrolyte data. The values of $G_s^0(CA)$ for the 20 salts were then fitted to eq. (4) using non-linear least squares [16] to extract the best values of δ_{sC} and δ_{sA} for a given set of ionic radii. Quite good fits of the experimental data to the MSA equation for the Gibbs energy of solvation of the 1-1 electrolytes formed from these simple ions were obtained for both sets of radii. However, on the basis of the estimates of the Gibbs solvation energies, the radii obtained from solution data are clearly preferred since the values of $G_s^0(i)$ are very close to experimental values of the real solvation energy for single ions [17,18], also tabulated by Parsons [4]. Of course, this quantity, which is equal to the negative value of the work function for the ion [19], contains a contribution from the surface potential of water which is estimated to be approximately 130 mV at 25 °C [4, 20]. As a result, the experimental real potential is about 12.5 kJ mol⁻¹ less negative than the single Gibbs energy of solvation for cations, and about 12.5 kJ mol⁻¹ more negative for anions. Considering the analytical simplicity of the MSA expression for the Gibbs solvation energy, the present results are indeed very gratifying. Using the single ion data, one may estimate a value for the constant required to convert the data on the scale referenced to $G_s^0(H^+) = 0$ to an absolute scale. In the case of the radii based on diffraction data, the resulting constant is -1091 ± 7 kJ mol⁻¹ which compares well with the best value for the real potential of the H⁺ ion (-1088 ± 2 kJ) [17, 18]. Thus, the results reported here provide an acceptable basis for calculating single electrode potentials.

The present analysis was carried further by examining the data for the entropy of solvation of the same ions in aqueous solutions using eq. (6). Tabulated values for this quantity are also referenced to the solvation entropy of the hydrogen ion ($S_s^0(H^+) \equiv 0$) [4]. Keeping this in mind, eq. (6) can be rewritten as

$$Y = -S_s^0(H^+) \left(1 - \frac{1}{\epsilon_s}\right) - \frac{d\delta_s}{dT} X \quad (7)$$

where

$$Y = \Delta S_s^0(i) \left(1 - \frac{1}{\epsilon_s}\right) + \frac{G_s^0(i)}{\epsilon_s} \frac{d\epsilon_s}{dT}, \quad (8)$$

$$X = \frac{8\pi\epsilon_0}{N_0(z_i e_0)^2} [G_s^0(i)]^2, \quad (9)$$

and $\Delta S_s^0(i)$ is the tabulated entropy of solvation referenced to that for H^+ ion. The variables X and Y were calculated using the best values of the Gibbs solvation energies from Table 1. A plot of the data for the alkali metal cations is shown in Fig. 1, an excellent linear correlation being obtained ($r = 0.993$). The resulting value of $S_s^0(H^+)$ estimated from the intercept is $-126 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$; this agrees quite well with the value estimated by Conway ($-131 \text{ J K}^{-1} \text{ mol}^{-1}$) [1]. The value of $d\delta_{sC}/dT$ obtained from the slope is 0.029 pm K^{-1} . A more important test of the present model is the comparison with results obtained from the analysis of data for anions. The corresponding plot for the halide ions is also shown in Fig. 1. The linear correlation in this case is not as good ($r = 0.988$), and the estimate of $S_s^0(H^+)$ is $-112 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$. Keeping in mind that data are available for only four ions this result agrees reasonably well with that based on the alkali metal halide data. Estimates of $S_s^0(H^+)$ based on the Pauling radii are farther from the estimate of Conway [1] and farther from each other when one compares cationic and anionic data; therefore they are considered less reliable. Finally, the value of $d\delta_{sA}/dT$ estimated from the slope of the plot for the anionic data is 0.047 pm K^{-1} . Just as the values of δ_s are different for cations and anions, so are their temperature coefficients.

Discussion

The above analysis demonstrates that the MSA provides an excellent description of the thermodynamic properties for simple monovalent ions in aqueous solution. Having chosen a set of ionic radii, only two additional adjustable parameters are required to achieve a fit with experimental data for the Gibbs solvation energy, namely, the MSA distances for cations and anions. It should be emphasized that the values of this parameter reported here are quite different from that obtained from the Wertheim equation which gives an estimate of 51.6 pm for water at 25 °C when the

molecular diameter is assumed to be 274 pm. As one would expect, small differences in δ_s lead to large changes in the estimates of $G_s^0(i)$. These differences are attributed to the fact that the original Wertheim model represents the pure solvent as a collection of hard spheres with point dipoles. Although estimation of δ_s on the basis of eq. (3) accounts for some of the other electrostatic interactions between solvent molecules, this value does not account for the more complex aspects of ion-dipole interactions in electrolyte solutions. This is most easily seen when one recognizes that the solvation of cations and anions with equal radii is not the same. Thus, the present empirical approach to dealing with the "stickiness" of these interactions seems appropriate when one considers the complexity of the theory that would be required to provide an adequate description including higher order electrical moments and polarizability.

It is also apparent from the present analysis that the choice of ionic radii used in estimating the thermodynamic properties is extremely important. It is also not surprising that the best fit between theory and experiment was obtained using the radii from diffraction experiments. In our previous analysis of the data for the Gibbs solvation energy, the single ion values estimated by Conway [1] and Pauling radii were used to obtain the best fit between the experimental data and the MSA model. However, the present method of separating the cationic and anionic components using thermodynamic data for the salts provides an extrathermodynamic route to the single ion data and produces results which are much closer in agreement with the real solvation energy data of Randles [17]. The uncertainty in most radii used to obtain this separation is in the order of ± 10 pm. As more data are gathered from the diffraction experiments, the resulting estimates of r_i should improve and may provide a better description of the single ion quantities.

In order to estimate the entropy, and eventually the enthalpy of solvation, two more parameters are required, namely, the temperature coefficients of the MSA distances for cations and anions. The present analysis requires that one uses estimates of the single ion Gibbs solvation energies to obtain these parameters and yields excellent results. The major point of weakness in the analysis is uncertainty in the values of r_i . Thus, improvement in these estimates should lead to

results from the entropic analysis which agree with one another when one compares data for cations and anions.

The present analysis for the aqueous solvation data can easily be extended to other polar solvents using data for the Gibbs energy and entropy of transfer of simple 1-1 electrolytes composed of alkali metal cations and halide anions. Unfortunately, these data are usually available for less than ten electrolytes from the group considered here [12, 21]. This means that the chances of obtaining an unambiguous fit using non-linear least squares are smaller. However, such an analysis would be very helpful mainly because it would allow one to assess the TATB assumption which has been predominantly used to separate cationic and anionic components for thermodynamic transfer data [12, 13]. This assumption is based on equal solvation of large ions, namely, the tetraphenylarsonium cation and the tetraphenylborate anion. On the basis of the MSA, equal solvation of these ions would require not only that their effective radii be equal, but also that their MSA parameters be the same. Since these ions are tetrahedral and not spherical, the stated conditions may be met. Separation of the cationic and anionic components of thermodynamic parameters for simple electrolytes on the basis of the present model would provide an acceptable alternative by which the TATB assumption could be tested. This subject will be dealt with in detail in a future paper.

Acknowledgement

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Table 1. Values of Ionic Radii, MSA Parameter δ_s and Estimated Gibbs Energy of Solvation for the Alkali Metal Cations and Halide Anions

Ion	Pauling		Diffraction Data	
	r_i / pm	$-G_s^0(i) / \text{kJ mol}^{-1}$	r_i / pm	$-G_s^0(i) / \text{kJ mol}^{-1}$
Li^+	60	481	71	503
Na^+	95	386	97	423
K^+	133	318	141	332
Rb^+	148	298	150	319
Cs^+	169	273	173	288
F^-	136	445	124	432
Cl^-	181	345	180	320
Br^-	195	322	198	295
I^-	216	293	225	264
MSA Parameter		δ_s / pm		δ_s / pm
Cations		82.4		65.3
Anions		18.0		34.6
Standard Deviation for fit to eq. (4)		1.5 kJ mol^{-1}		1.1 kJ mol^{-1}

Legends for Figures

Figure 1. Plot of entropy of solvation corrected for long range electrostatic effects, Y (eq. 8) against X , a quantity proportional to the square of the Gibbs solvation energy (eq. 9) for the alkali metal and halide ions in aqueous solutions.

